MEIGS (J. Aitken)

Essay on the relation of atomic heat
to crystalline form ~ ——— ———

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Essay on the relation of atomic heat

ESSAY

ON THE

RELATION OF ATOMIC HEAT TO CRYSTALLINE FORM.

BY

J. AITKEN MEIGS, M. D.

"CRYSTALLIZATION is a peculiar and most admirable work of nature's geometry, worthy of being studied with all the power of genius, and the whole energy of the mind, not on account of the delight which always attends the knowledge of wonders, but because of its vast importance in revealing to us the secrets of nature; for here she does, as it were, betray herself, and, laying aside all disguise, permits us to behold, not merely the results of her operations, but the very processes themselves." GULIELMINI.

"Although sound logic and natural philosophy forbid us to base lofty edifices of theories and laws upon but few observations; on the other hand it compels us not to be satisfied, like the mason, with the mere collection of the building-stones, and to lose sight, over accumulating details, of a higher object, but at certain stages to look around, to arrange the results obtained, to compare them with known phenomena, and thus to extend our intellectual horizon." DR. CARL SCHMIDT, *Comp. Phys. of the Invertebrata.*
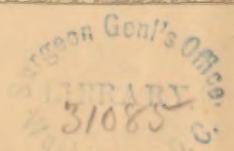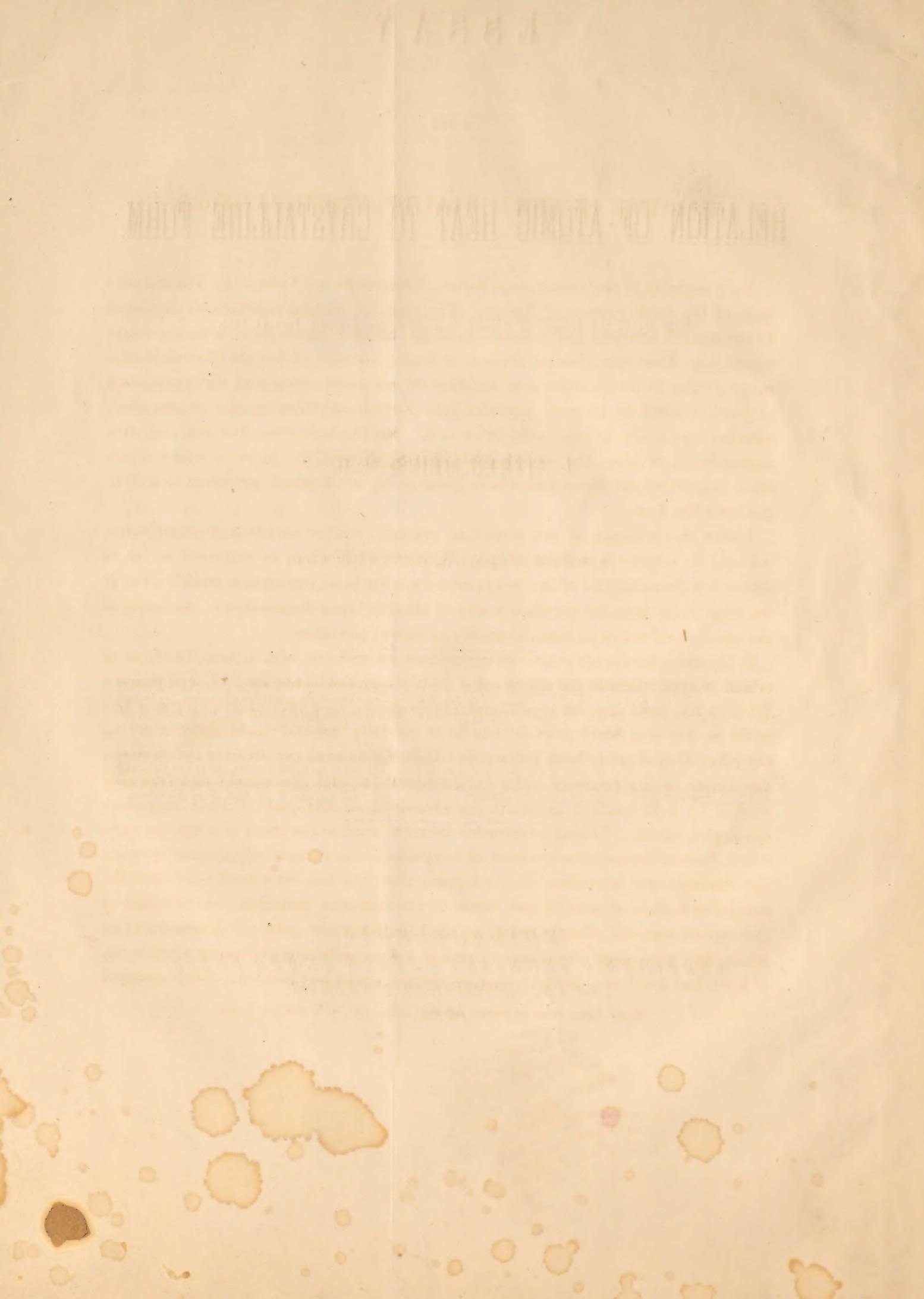
RELATION OF ATOMIC HEAT TO CRYSTALLINE FORM.

Very probably in the atomic constitution of matter we are to seek the true material basis of the whole Science of Nature. The unity of Natural Science—as displayed in the mutual relations and connections of its different parts—here finds a positive expression. Therefore, Natural Science, as a unit, becomes philosophically intelligible in proportion to the clearness and accuracy of our views concerning the aggregation of passive atoms or ultimate particles into Forms,—whether organic or inorganic, whether specifically or generically impressed. But the comprehensive study of such aggregations, requires the contemporary investigation of the physical agent which brings together inert atoms and retains them in contact,—which preserves as well as produces the form.

Under the influence of the attractive principle, matter everywhere tends determinedly to assume a definite shape. Hence crystallization is perceived to be as common a characteristic of the inorganic, as vitality is of the organic world. Yet if we may judge from the standard works of the day, upon these subjects, the cause of the one is involved in as much obscurity as that of the other.

A crystal is inanimate matter individualized, or endowed with a form, in virtue of which it approximates the unorganized to the organized kingdom. The difference between the most complex crystal and the simplest plant is of course extreme; but while on the one hand physiologists have carefully detailed these differences; on the other, they seem to have lost sight of the striking analogies which exist between the *seriate* results produced alike in the crystalline and the animal and vegetable worlds, by a methodical intermittency of action, on the part of their respective developing agents. Thus the concentric layers of wood in the trunk of a tree, between which lines of demarcation are more or less evident,—as is especially the case between the duramen and alburnum of the lignum vitæ and the coco-wood,—indicate the successive periods of activity and repose of the formative principle. So the lines of cleavage in a crystal silently assure us that the attractive power is intermittent in action, and that along these weak planes it had ceased its exertions for a while, or, at least, had acted very feebly.* Among the numerous and beautiful forms assumed

* Dana. Amer. Journ. of Science and Arts, 2d ser., vol. iv., p. 378,—v., p. 100.

by snow-crystals, we find specimens from whose primitive rays are given off lateral spines or branchlets in pairs, directly opposite to, and separated the same distance from each other. One basal ray with its secondary spines is the fac-simile of all the rest. Now this tendency to the repetition of precisely similar parts is seen not in the formation of a crystal only, but also in the development of the highest plants, in zoophytes and in the lower mollusca and articulata where it embraces entire groups of organs. Thus in the highest forms of the Echinodermata, five precisely similar rays are developed around a common centre. The same tendency is seen in the eight or ten tentaculæ which surround the mouths of the dibranchiate Cephalopoda. Similar examples are presented by the Annelida. In all these instances it is evident that the developing force has acted methodically from a common centre, towards the accomplishment of a definite end or object—the production of a special form. In classification, form is of the highest value to the practical naturalist. But form is not fundamental, it is merely secondary; it is the effect of the action of the developing cause upon ponderable matter. Aided by a severe and cautious logic, the careful and elaborate study of comparative morphology, it is reasonable to hope, will enable us to advance from the known to the unknown, from the multitudinous forms of natural objects to their physical cause. Moreover, it will probably lead to the discovery of profound analogies between the organic and the inorganic worlds,—analogies manifested through similarity in the modes of action of the formative or developing principle.

Crystallization naturally constitutes the first chapter in the history of comparative morphology. A knowledge of crystallization is of prime importance to the chemist and mineralogist in assisting them to arrange bodies in their natural groups; to the natural philosopher in elucidating the laws of cohesive attraction; to the physiologist, since it promises to throw considerable light upon the function of a fundamental physical agent, the analogy of whose method of action with that of the developing principle in the organic world, will lead, if not to their identification, at least to more definite knowledge of the phenomena of growth; to the physician, as it affords some clue to the pathology of symmetrical diseases; and lastly to the philosophic naturalist, from its relation to organic morphology, through which, perhaps, will be attained that much desired result, the demonstrative proof of a great general or archetypal plan of organization.

A diligent and attentive inquiry into the rationale of the phenomena of isomorphism and dimorphism would dissipate much of the mystery that hovers about the cause of crystallization in general; and even, perhaps, illuminate many obscure parts of organic science.

Towards the accomplishment of so desirable a result, an important step was made

by Mitscherlich, who from his elaborate researches deduced the well-known law, that the same number of atoms combined in the same way produce the same crystalline form, and that crystalline form is independent of the chemical nature of the atoms, and determined by their number and relative position only. Carefully considered, however, this law is seen to reveal merely the secondary or proximate cause of any special crystalline form. It does not distinctly explain the phenomenon of isomorphism. Obviously in the power which aggregates the atoms, we are to look for the prime cause of crystallization in general. Mitscherlich's law does not clearly explain why different acids having different atomic weights and volumes, should, when combined with the same base, present the same geometrical figure. According to the atomic theory, the ultimate atoms composing the various chemical elements differ in weight and volume. The numbers expressive of atomic weight are in some measure indicative of atomic magnitude, otherwise the present great diversity in the atomic numbers of the elements and their compounds could scarcely exist. And this supposition receives very strong support from the well-known, but not duly appreciated fact, that the atomic weight of a body may be very great, while its atomic number is very small. Keeping in view this difference in atomic magnitude, it is difficult to conceive, as indeed has been objected to Mitscherlich's law, why arsenic and phosphoric acids, whose respective atomic weights are 115 and 71, should, when combined with soda, produce isomorphous compounds; why the seleniate and sulphate of soda should be identical in form, when the atomic weight of selenic acid is 64, and that of sulphuric acid 40, &c.

Again, it is a well-known fact that the same body may assume two or more distinct and unrelated forms. Thus, carbon presents us with regular octohedrons in the diamond, and six-sided plates in graphite, or plumbago. Sulphur is also dimorphous, assuming two incompatible crystalline forms. The minerals rutile, brookite and anatase are distinct crystals of titanic acid. Carbonate of lime, too, expresses itself dimorphously. Such facts as these show that as far as ponderable elements are concerned, crystalline form is by no means the consequence of an invariable atomic constitution. Moreover, isomorphism is compatible with a considerable difference in the number of atoms. Thus, according to Mitscherlich, sulphur in one of its forms is isomorphous with the bisulphate of potassa. The nitrite and the nitrate of lead have the same octohedral figure, yet the latter compound has two atoms more of oxygen than the former. Gmelin instances a number of similar examples.

Here, then, it remains to be explained why two or more acids having different atomic weights, upon uniting with the same base, assume the same crystalline form; why the same body presents us with examples of dimorphism, trimorphism, or even, as in the case of water, of polymorphism; why some substances are isomorphous both in the separate state and in combination; and lastly, why some substances replace

each other in compounds according to equal, and others according to unequal numbers of atoms.

In 1809, from his own experiments, and those performed in company with Humboldt, Gay Lussac clearly demonstrated that gases combine with each other by definite volumes as well as by definite weights, and that the volume of a gaseous compound is distinctly related to that of one or both of its constituents. Prout, Thompson and others, by their researches, afterwards showed that this law embraced vapors, and also the vapors of certain bodies which possess the elastic form only when combined with permanent gases.

Recently Dr. Hermann Kopp of Giessen has attempted to extend the volume-theory in another direction. He endeavors to show,—and with remarkable success,—that all bodies in forming chemical compounds, unite by definite volumes in addition to equivalent weights; that every body, whether elementary or compound, has a specific atomic volume; that as atomic weights are proportional, so are atomic volumes; that whilst atomic weight gives us the idea of mass, a crystal is the representative of a regular and definite volume. From considerations of this nature he enunciates the following law: " The specific weight of isomorphous bodies is proportional to their atomic weights; or, isomorphous bodies possess the same atomic volume."*

From the numerous examples adduced by Kopp, of the validity of this law, we may legitimately infer that the phenomenon of isomorphism may be expressed by saying, that many elementary and compound bodies tend strongly to assume the same, or, at least, but a slightly differing volume. Furthermore, all crystallization is the assumption of a form or regularly defined volume, the specifically regular outline or contour of which is dependent upon the power and freedom of the aggregating force. In the study of the volume of a body, then, is in all probability involved the study of the cause of cohesive attraction, isomorphism, dimorphism, trimorphism, polymeric-isomorphism, and all the interesting though obscure phenomena of crystallization. Evidence of a very high character exists for supposing that identity in the arrangement of atoms is the immediate predisposing cause of identity in form or volume. Sameness in number does not appear necessary, for examples exist of isomorphous bodies having unequal numbers of atoms. Reasoning in this channel, we are constrained to seek for the cause not only of isomorphism, but of all crystallization, in that force, whatever it may be, which is capable of arranging an equal or unequal number of atoms into the same volume. Now, many crystals, when once formed, will maintain themselves unchanged under very varying external conditions. Hence it may be inferred that the force which gave form to a portion of matter, which created the crystal, so to speak, must exist with and in it, otherwise that form could not be preserved. Just as in the organic world, the parent imparts its vital powers

* London Philosophical Magazine, 3d series, Vol. 18, p. 255.

to the ovum, which, through the processes of development, growth and nutrition, is seen to act as a preservative power; when it departs, the mass of organized particles which it vivified or animated is left a prey to surrounding destructive influences.

A crystal is composed of ponderable and imponderable elements;—the former visible, gross and inert; the latter invisible, subtle, expansive and self-repellant. This imponderable is caloric, and in one of its relations it constitutes the specific heat of a body. Through all ponderable bodies it diffuses itself without exception, and accumulates in quantities varying with the peculiar nature of the ponderable substance with which it is combined. Here the question naturally presents itself to the inquiring mind, as to the *cui bono* of this caloric, its uses and relations. Its continued presence, and well-known power and activity, as compared with ponderable matter, authorize us to conclude that it is not without use, otherwise we accuse nature of superfluity, of supererogation, which is manifestly unphilosophical. The combined heat of a body, we know, is intimately connected with the existing condition or state of aggregation of that body. Variation in the one is attended with alteration in the other. Ice, water and steam are three very different forms of one and the same gaseous compound. In all, the ponderable atomic constitution is the same, but the amount of heat contained in each is very different. Diminish the heat of steam, and you convert it into water; diminish it still further, and you convert the water into ice. In this simple instance, then, and others could easily be furnished, we have beautifully manifested the extraordinary influence of caloric upon the aggregation of atoms. And yet with so simple and forcible an example before them—an example embracing the three known conditions in which it is possible for ponderable matter to exist—chemists still express themselves doubtfully as to the propriety of admitting heat as an active constituent of bodies equally essential as their ponderable elements.

In his interesting paper above referred to, Kopp has given us numerous examples which tend strongly to substantiate the relation which he contends for between isomorphism and sameness of atomic volume. Crystalline form and volume of atoms are thus closely assimilated, if not, indeed, identified. Thus far concerning the ponderable matter. Philosophical confidence in the intelligential character and immutability of nature's laws, and in the unerring exactitude of the results of those laws,—in other words, implicit faith in the fundamental and truly scientific doctrine that "nothing was made in vain," here encourages us to advance at least one step further in the cautious investigation of this intricate subject, by attempting to ascertain the relation between the atomic volume and the imponderable element caloric surrounding the atoms of a crystal.

In the following tables, where a number of elementary and compound bodies have been grouped together isomorphously, it will be seen that for each group the numbers expressive of the atomic volumes of the different substances of that group are either

almost identical, or related to each other in a simple, multiple proportion.   A still
more evident similarity prevails throughout the numbers indicating the atomic heats
of the same bodies.   Furthermore, a remarkable relation, in some instances more
manifest than in others, is observed to exist between the atomic heat of a body and
its atomic volume.

The first column of the table contains the names of the substances, or, when these
are compound, their formulæ only; the second, their atomic weights upon the hydro-
gen scale; the third, their specific gravities; the fourth, the observed specific heats,
with the initials of the Experimenters attached; the fifth, the mean specific heats;
the sixth, the atomic heats obtained, after the manner of Dulong and Petit, by multi-
plying together the atomic weight and the specific heat; the seventh, the atomic
volumes, calculated according to the method of Schroëder and Kopp, by dividing the
atomic weight by the specific gravity.

Av. denotes Avogadro; Dl., Dalton; D,M., De la Rive and Marcet; Hm., Hermann;
Nm., Neumann; P,D., Petit and Dulong; Pr., Potter; P,J., Playfaire and Joule;
Rg., Regnault.

The specific gravities adopted are generally the means of the observations made by
Kopp, Karsten, Brisson, Gay Lussac and Thenard, Mohr, Breithaupt and others, the
results of whose experiments are recorded in the more elaborate chemical works.

ELEMENTARY BODIES.

Elements.	Atomic Weight	Specific Gravity.	Specific Heat.	Mean Specific Heat.	Atomic Heat.	Atomic Volume.
Sulphur	16	1.99	0.1880 P,D. 0.1900 Dl. 0.2026 Rg. 0.2090 Nm.	0.1974	3.2416 Rg. 3.15840	8.04
Selenium	40	4.31	0.0675 Hm. 0.0884 D,M. 0.0837 Rg.	0.0782	3.3480 Rg. 3.1280	9.28
Tellurium	64	6.26	0.0515 Rg. 0.0912 P,D.	0.0713	3.2960 Rg. 4.5632	10.22
Manganese	27.8	8.02	0.14411 Rg.		4.00598	3.466
Iron	27.2	7.73 7.13 P,J.	0.1054 Hm. 0.1100 P,D. 0.1130 Pr. 0.1138 Rg. 0.1300 Dl.	0.1144	3.09536 Rg. 3.1116	3.518 3.675 P,J.
Cobalt	29.6	8.57 7.989 P,J.	0.1070 Rg. 0.1172 D,M. 0.1498 P,D.	0.1246	3.1672 Rg. 3.6881	3.453 3.675 P,J.
Nickel	29.6	8.46 7.832 P,J.	0.1035 P,D. 0.1086 Rg.	0.1060	3.21456 Rg. 3.1376	3.498 3.675 P,J.
Copper	31.8	8.896 8.424 P,J.	0.0949 P,D. 0.0950 D,M. 0.0951 Rg. 0.0960 Pr. 0.0961 Hm.	0.0954	3.02418 Rg. 3.0337	3.574 3.675 P,J.
Zinc	32.3	6.99 7.21 Bz.	0.0927 P,D. 0.0929 Nm. 0.0940 Pr. 0.0955 Rg. 0.1000 Dl.	0.0950	3.08465 Rg. 3.0590	4.620 4.479 Bz.
Cadmium	55.8	8.63	0.0385 Hm. 0.0567 Rg. 0.0576 D,M.	0.0509	3.16386 Rg. 2.8402	6.465
Barium Strontium Lead	68.6 44 103.8	3.75 2.542* 11.35	0.0293 P,D. 0.0299 Hm. 0.0314 Rg. 0.0320 Pr. 0.0400 Dl.	0.0325	3.25932 Rg. 3.3735	9.145
Tin	59	7.29	0.0514 D,M. 0.0515 P,D. 0.0560 Pr. 0.0562 Rg. 0.0700 Dl.	0.0570	3.3158 Rg. 8.3630	8.093
Titanium	24.3	5.29				4.593

* Bunsen. Comptes Rendus, Avril, 1855, p. 717.

Elements.	Atomic Weight.	Specific Gravity.	Specific Heat.	Mean Specific Heat.	Atomic Heat.	Atomic Volume.
Platinum	98.8	21.5	0.0314 P,D. 0.0324 Rg.	0.0319	3.20112 Rg. 3.15172	4.595
Palladium	53.4	11.7	0.0593 Rg.	...	3.1666 Rg.	4.564
Iridium	98.8	21.6	0.0368 Rg.	...	3.63584 Rg.	4.574
Osmium	99.7	21.8	...	...	...	4.573
Tungsten	95	17.3	0.0350 D,M. 0.0364 Rg.	0.0357	3.3915	5.491
Molybdenum	48	8.63	0.0659 D,M. 0.0722 Rg.	0.0690	3.3120	5.561
Gold	199	19.258	0.0298 P,D. 0.0324 Rg. 0.0340 Pr.	0.0320	6.3680	10.333
Silver	108.1	10.428	0.0557 P,D. 0.0570 Rg. 0.0590 Pr.	0.0572	6.1833	10.366
Sodium	23.3	0.97	...	...	...	24.123
Potassium	39.2	0.86	...	...	...	45.581
Phosphorus	31.4	1.77	0.1887 Rg. 0.2900 Hm. 0.3850 Av.	0.2879	5.92518 Rg. 9.0400	17.740
Arsenic	75.2	5.74 5.23 P,J.	0.0804 Hm. 0.0810 Av. 0.0814 Rg.	0.0809	6.0836	13.101 14.378 P,J.
Antimony	129	6.72	0.0470 Nm. 0.0496 Hm. 0.0508 Rg. 0.0520 Pr.	0.0498	6.4242	19.196
Bismuth	106.4	9.79	0.0270 Nm. 0.0288 P,D. 0.0308 Rg. 0.0330 Pr.	0.0299	3.1813	10.867
Iodine	126	4.948	0.0541 Rg. 0.0890 Av.	0.0715	9.0090	25.464 26.220
Bromine	78.4	2.99	0.1350 D,M.	...	10.5840	

COMPOUND BODIES.

Formulæ.	Atomic Weight.	Specific Gravity.	Specific Heat.	Mean Specific Heat.	Atomic Heat.	Atomic Volume.	Volume according to Kopp.
$Sn\,O_2$	75.	6.960	0.0933 Rg. 0.1110 Av. 0.0900 Hm. 0.0931 Nm.	0.0968	7.260	10.775	134.38
$Ti\,O_2$	40.5	3.792	0.1716 Rg. 0.1630 Hm. 0.1703 Rg. 0.1724 Nm.	0.1693	6.856	10.680	132.82
Al_2O_3	51.4	3.833	0.1963 Hm. 0.2000 Av. 0.1942 Nm. 0.1976 Rg. 0.1972 Nm. 0.2173 Rg.	0.2004	10.3005	13.409	168.07
Fe_2O_3	78.4	5.254	0.1757 Rg. 0.1681 Rg. 0.1669 Rg. 0.1692 Nm.	0.1699	13.3201	14.921	186.23
Cr_2O_3	80.2	5.21	0.1796 Rg. 0.1960 Nm. 0.2126 Hm.	0.1961	15.7272	15.393	192.63
MgO, CO_2	42.7	2.834	0 2220 Nm.	...	9.4794	15.067	181.25
FeO, CO_2	57.2	3.800	0.1934 Rg. 0.1820 Nm.	0.1877	10.73648	15.052	188.50
$\frac{1}{2}\left\{\begin{array}{l}MgO, CO_2 \\ CaO, CO_2\end{array}\right\}$ *	46.6	2.884	0.2174 Rg.	...	10.13084	16.158	202.36
CaO, CO_2	50.5	2.735	0.1945 Hm. 0.2046 Nm.	0.1995	10.0747	18.464	231.20
CaO, CO_2	50.5	2.963	0.2018 Nm. 0.2085 Rg.	0.2051	10.3575	17.043	213.47
SrO, CO_2	74.	3.615	0.1445 Nm. 0.1448 Rg.	0.1446	10.7004	20.470	255.53
BaO, CO_2	98.6	4.301	0.1078 Nm. 0.1104 Rg.	0.1091	10.7572	22.924	286.71
PbO, CO_2	133.8	6.446	0.0860 Rg. 0.0814 Nm. 0.0818 Hm.	0.0830	11.1054	20.601	259.20
BaO, SO_3	116.6	4.323	0.1088 Nm. 0.1128 Rg.	0.1108	12.9192	26.971	337.55
SrO, SO_3	92.	3.770	0.1356 Nm. 0.1428 Rg.	0.1392	12.8064	24.403	305.30
PbO, SO_3	151.8	6.233	0.0872 Rg. 0.0848 Nm.	0.0860	13.0548	24.354	304.14

* Dolomite.

Formulæ.	Atomic Weight.	Specific Gravity.	Specific Heat.		Mean Specific Heat.	Atomic Heat.	Atomic Volume.	Volume according to Kopp.
BaO, NO₅	130.6	3.050	0.1334 Hm. 0.1523 Rg.		0.1428	18.6496	42.819	536.75
SrO, NO₅	106.	2.948	0.1683 Hm.		…	17.8398	35.956	449.41
PbO, NO₅	165.5	4.584	…		…	19.2*	36.103	452.58
Ba Cl	104.	3.782	0.0780 Hm. 0.0896 Rg.		0.0838	8.7152	27.498	343.75
Sr Cl	79.4	2.803	0.0972 Hm. 0.1199 Rg.		0.1085	8.6149	28.326	353.18
Pb Cl	139.2	5.574	0.0664 Rg.		…	9.2428	24.973	312.24
Ca Cl	55.9	2.127	0.1642 Rg.		…	9.1787	26.281	…
KO, NO₅	101.2	2.030	0.2690 Av. 0.2387 Rg.		0.2538	25.6845	49.852	624.71
NH₄O, NO₅	80.	1.643	…		…	30.4*	48.691	612.00
NaO, NO₅	85.2	2.185	0 2400 Av. 0.2782 Rg.		0.2591	22.0753	38.993	489.08
AgO, NO₅	170.1	4.355	0.1435 Rg.		…	24.109	39.058	488.79
Na Cl	58.6	2.114	0.2210 Av. 0.2300 Dl. 0.2140 Rg.		0.2216	12.9857	27.719	347.09
Ag Cl	143.5	5.363	0.0844 Hm. 0.0911 Rg.		0.0877	11.7849	26.757	334.81
KO, SO₃	87.2	2.640	0.1690 Av. 0.1901 Rg.		0.1795	15.6524	33.030	413.25
KO, CrO₃	99.3	2.652	0.1850 Rg.		…	18.370	37.443	468.33

To the first group belong sulphur, selenium and tellurium, substances closely connected, not only by their own similarity in chemical properties, but also by that of their analogous compounds. Sulphur and selenium, although their atomic weights, and therefore the magnitude of their atoms, differ so much, correspond very closely, nevertheless, in both atomic heat and volume. Hence, probably, the isomorphism of the sulphates and seleniates, sulphurets and seleniurets—a point which I have not been able to verify satisfactorily, in consequence of not being able to find upon record any reliable specific heats for the seleniates and seleniurets, by which they might be compared with the corresponding sulphur salts. The atomic volume of Pb S is 16.592; that of Pb Se, 16.341. The experiments of Mitscherlich show that the sulphates and seleniates crystallize in right, rhombohedral prisms, at a very low temperature; in octohedrons with a square base, at a mean temperature; and in oblique prisms, at a

* Calculated according to the method laid down by Gmelin.

very elevated temperature. Tellurium associates itself with this class by heat and volume, as well as by chemical properties. Reasons exist for ranking oxygen with these three elements. The probability of such a connection finds some support in the fact that the combining measure of aqueous vapor and sulphuretted hydrogen is two volumes, and that of the oxide, sulphuret and telluret of ethyl, four volumes. An atom of each of the two former substances, probably possesses a heat-sphere of the same size. The calorific envelopes of the atoms of the last three are also equal to each other in extent, but twice as great as those of the former. The relation of the oxides and sulphurets is seen in the subjoined table.

Oxides.	Atomic Heat.	Atomic Volume.	Sulphides.	Atomic Heat.	Atomic Volume.
HgO	5.665827	9.855	HgS	6.00736	14.625
MnO	5.58956	7.568	FeS	5.97080	...
CuO	5.65199	6.297	NiS	5.84273	...
NiO	5.97276	...	CoS	5.70548	...
MgO	5.71320	6.500	ZnS	5.93005	12.286
ZnO	5.98176	7.178	PbS	6.09303	16.592
PbO	5.72192	11.982	SnS	6.27375	...
CaO	5.10150	9.016			
SnO	6.2980	10.044			

Sulphuric and manganic acids are isomorphous. From this is inferred the isomorphism of the elements sulphur and manganese. Hence manganese is regarded as the connecting link between the first three elements in the table, called the sulphur class by Graham, and the next seven, named the magnesian class. Manganese is regarded, therefore, as a sort of transition element, by which one group runs into or is blended with the other,—a good example of the artificiality or unreality of scientific classification in general. For the great plan of nature is, in the main, so uniform, that the gaps which apparently dissociate the different parts are being constantly filled up as new discoveries are made. Now, manganese has an atomic heat of 4.0059, and an atomic volume of 3.466. The first connects it, therefore, with both groups, and the last with the magnesian series. The mean atomic volume of most of the bodies in the second class, is a multiple by three of that of the first; the others bear an equally simple relation. The correspondence of their elements in heat and volume, is of itself sufficient to bring these two classes into one category. Moreover, their more perfectly isomorphous protoxides evince a similar relationship in heat and volume, as shown in the second table. It may be interesting to observe in this connection that ice (HO) and protoxide of zinc, (ZnO) which differ not much in atomic heat, have been seen to assume the same regular, six-sided form. Their complete isomorphism, however, has not yet been established by exact measurement.

	At. Heat.	At. Volume.
HO	6.480	9.8
ZnO	5.98176	7.178

As oxygen, through the resemblance of certain oxides and sulphurets, appears to

rank with sulphur, so the resemblance in their chemical relations between HO and CuO is supposed to connect hydrogen with the group in question. It is curious to observe that the atomic heat and volume of HO tend to confirm the notion of its connection with the magnesian class.

Lime (CaO) probably occupies an intermediate position between this and the barium series, blending them gradually together. This is very well shown in the table of isomorphous salts, in the two groups of carbonates, where carbonate of lime as calc-spar, assimilates, on the one hand, with the corresponding carbonates of magnesia. iron, the mineral dolomite, &c., and on the other, as arragonite, identifies itself with the carbonates of strontia, baryta and lead. The protoxides of barium, strontium. calcium and lead, are nearly related in heat and volume. But the similarity of the barium class to the magnesian is shown through their chlorides, where the correspondence in atomic heat and volume is quite remarkable.

Salts.	Atomic Heat.	Atomic Volume.
BaCl	9.31528	27.513
SrCl	9.52006	28.357
CaCl	9.17878	26.244
MgCl	9.36026	...
MnCl	8.98065	...
ZnCl	9.20577	...
SnCl	9.59198	...
PbCl	9.24427	25.217
HgCl	9.42415	25.714

In the next two groups the numbers for atomic heat are the same throughout; as. with one exception, are those for atomic volume. This is an exception in appearance only, and not in reality, for its volume-number is just about double that of the others. preserving, therefore, a simple multiple relation. This view finds confirmation in the isomorphism of the oxides of tin and titanium, which compounds, as the table shows. are sufficiently identified in heat and volume. Indeed the coincidence is still more positive than at first sight appears. It will be seen that the specific heat obtained by Avogadro for SnO_2 differs so much from the other three observations, that it may very properly be omitted in calculating the mean specific heat of this body. This procedure will give 6.9075 for the atomic heat of the oxide of tin. So the number furnished by Hermann for the specific heat of TiO_2 may, with equal propriety, be rejected in ascertaining the mean specific heat of titanic acid. We thus obtain 6.9417 for the atomic heat of this latter substance. These two numbers may be considered as identical. I may here remark that a similar analysis of the whole table would lead to results still more striking than those indicated. I have preferred, however. to give all the recorded specific heats, with the mean for each elementary and compound substance, from which to calculate the atomic heat, because in this manner is avoided the confusion of so many analogous numbers for any body, and still more because I regard the results obtained in the table as approximations merely to a great general truth or law in nature, which yet remains to be demonstrated by a logical

synthesis of scientific facts. In these investigations it must, for the present, be kept constantly in view, that the numbers obtained by experiment for the specific heat of different bodies, do not accurately express the amount of caloric combined with the ponderable matter of those bodies. The specific heat is only a portion of the whole quantity of combined heat; and, as Regnault has shown in his second memoir,* the obstacles to be overcome in obtaining the specific heat of any substance, with perfect accuracy, are exceedingly great, if not, indeed, insurmountable with our present appliances.

From the isomorphism of their double chlorides, Dr. Clark is inclined to associate the tin and platinum classes. The relation of these two series in heat and volume lends considerable support to their presumed affinity. According to Breithaupt, CdS is isomorphous with the alloy IrOs. The atomic volume of either iridium or osmium is to that of CdS as $1 : 1\frac{1}{2}$. Palladium, although not generally arranged in this series, appears here to find its natural place.

Tungsten and molybdenum correspond in heat and volume. The tungstates and molybdates are isomorphous, as their agreement in atomic volume sufficiently indicates. I have not been able to find upon record the atomic heat of these salts. Their supposed isomorphism is confirmed by the following comparison :—

	At. Heat.	At. Volume.
WO_3	9.496	22.580
MoO_3	9.533	20.809

The bisulphurets of tin and molybdenum, which present some resemblance in their physical constitution, have atomic heats but little different. The bisulphuret of iron differs very much from these in its characteristics, and we find that its atomic heat is also very different. (Regnault.)

In the metallic state gold and silver are isomorphous. Their relationship in heat and volume is very obvious. I have followed Gmelin in adopting 199 as the atomic weight of gold. If we assign it 99.6, as do some of the chemists, and halve the atomic weight of silver, for the cogent reasons advanced by Regnault, the above relation still holds good. Or, if we reject the suggestion of Regnault, it will be found that in heat and volume silver is the exact multiple by two of gold; so that in either case, the simplicity of relation (which in the present state of our knowledge of these subjects is all that we can contend for) is still preserved. Sodium allies itself with silver, as shown by the resemblance in atomic volume of their carbonates, sulphates, nitrates and chlorides. In all this series, as far as the specific heats have been obtained, the same correspondence in heat and volume is evident.

The atomic volume of sodium, as given in the table, is about one-half that of potassium. These volumes would be equalized by doubling the atomic weight of sodium ; and it is interesting here to observe that this alteration has been proposed by Dr. Clarke from theoretical considerations of a different character. The simplicity of relation is therefore evident.

* Annales de Chim. et de Phys., 3me sér., t. 1, p. 200.

It is well known that the potassa and ammonia salts exhibit very complete iso-morphism. This, indeed, might be inferred from the comparison of the nitrates of these bases, as shown in the table. Hence it is probable that potassium and ammo-nium, as has been suspected, are themselves isomorphous, notwithstanding that one atom of nitrogen and four atoms of hydrogen replace one of potassium in combination. I have not the data to compare them, either by heat or volume.

Phosphorus, arsenic, antimony and bismuth, constitute a natural group to which nitrogen is thought to belong. For the first three the atomic heat is about the same; the number for bismuth is about one-half that of the others. The relation between the atomic volumes is not so evident. If we follow the example of many of the European chemists, and halve the atomic weights of phosphorus, arsenic and antimony, a tendency to multiple relations between the atomic volumes will become more evident. This tendency is developed in their isomorphous compounds.

Compounds.	Atomic Heat.	Atomic Volume.
$As_2 O_3$	12.68371	26.810
$Sb_2 O_3$	13.78377	26.984
$Bi_2 O_3$	14.30929	27.976
$As_2 S_3$	13.94600	35.606
$Sb_2 S_3$	14.87331	37.263
$Bi_2 S_3$	15.62921	37.257
$As_2 Cl_6$	31.96886	...
$P_2 Cl_6$	28.83052	95.034
$3PbO, PO_5$	52.463	...
$3PbO, AsO_5$	32.804	...

Iodine and bromine are isomorphous throughout their whole combinations. Chlorine in certain respects is naturally associated with them. Their relation in heat and volume is seen below.

Compounds.	Atomic Heat.	Atomic Volume.
KBr	13.312	48.612
KI	13.530	50.322
KCl	12.902	38.955
NaBr.	14.061	...
NaI	12.950	...
NaCl	12.541	28.199
AgBr	13.782	29.355
AgI	14.420	41.699
AgCl.	13.073	26.086
PbBr	9.711	27.481
PbI	9.812	38.166
PbCl	9.244	25.217

The isomorphous and calorific correspondences between the different bodies composing each of the several groups of compounds, are sufficiently obvious to require no comment.

In most of the standard chemical works, the elements have been classified isomorphously, not so much from any proof that they individually present, as from the isomorphism of their compounds. The law promulgated by Mitscherlich naturally leads to such supposition and consequent classification. It must not be forgotten, however, that comparatively few of the elementary bodies are crystallizable, and that, therefore, we are in great measure deprived of the positive and demonstrative proof of the isomorphism of all the elements. Nevertheless, two-thirds of the crystallizable elements belong to the regular system, and are hence isomorphous the one with the other. Of these, however, some crystallize in other forms, under which they are isomorphous with elements belonging to other groups, as the Rhombohedral and Right Prismatic. Hence, from their arrangement into various isomorphous classes, and the resemblance between and apparent correlation of these classes, we fairly, though indirectly, infer, as highly probable, that the chemical elements, under certain favorable conditions, are capable of assuming the same form. Now, the approximation of many of these elements, in atomic heat and volume, certainly seems to confirm the reality of this isomorphism. It will thus be seen that the capacity for heat of elementary atoms is related through isomorphism only. Moreover, it will be observed among compound atoms, that although similarity in chemical constitution is, in general, accompanied by sameness in capacity for heat, yet examples exist of differently constituted bodies also presenting this similarity. This is an important fact and one worthy of close consideration, since it probably explains why one atom in a compound body will replace two or more atoms in another with which it is isomorphous. Thus Cu_2S and AgS are isomorphous. Here two atoms of copper replace one of silver, and yet retain the same form. Now the atomic heat of copper is about half that of silver. The atomic heats of the two sulphurets are as follows :—

				At. Heat.				At. Volume.
Cu_2S	.	.	.	9.647	.	.	.	13.528
AgS	.	.	.	9.258	.	.	.	18.116

Even if we adopt Regnault's suggestion, before alluded to, and write both substances according to the formula R_2S, the numbers for atomic heat will still be nearly the same.

Bisulphuret of iron Fe_2S_4 is dimorphous. In the mineral Spirkise it is isomorphous with arsenide of iron Fe_2AsS_2. In the pentagonal dodecahedron of the regular system it is isomorphous with cobalt glance, CO_2AsS_2. Again, Cd_2S_2 and Ni_2S_2 are each isomorphous with Ni_2As. Thus it would appear that one equivalent of arsenic is isomorphous with two of sulphur. Now the table shows us that the atomic heat of

arsenic is about twice that of sulphur.   The atomic heat of Fe_2S_4 is 15.60384, of Fe_2AsS_2, 16.35392.   The cyanides replace the chlorides, three atoms occupying the space and performing the function of one.   The atomic heat of cyanogen is 14.4222, that of chlorine, 14.4627.

We come now to inquire why the atomic heat and volume in many of the isomorphous groups are not absolutely identical.   Many bodies called isomorphous are not strictly so.   Their corresponding angles sometimes vary several degrees.   A variation of 59′ has been observed by Mitscherlich in the analogous angles of different specimens of the same salt.   In the sulphates of barytes and strontia the angles of the rhombs differ by 2° 48′; in the carbonates of lime and magnesia by 2° 36′; and in the sulphates of zinc and magnesia by 38′.   Inequalities also exist between the axes of such plesimorphic bodies.   Now the interdependence of crystalline condition and atomic volume has been well and beautifully shown by Kopp, as the result of an attentive study of the various classes of plesimorphic and strictly isomorphic compounds.   That careful physicist found that variations in the individual angles of a crystal were accompanied by corresponding variations in its atomic volume.   But the angular value of a crystal depends upon the proportions between its axes, and these cannot suffer alteration without changing the density, and, consequently, its specific gravity—alterations necessarily preceding variation in atomic volume.   Elongation of the principal axis increases the atomic volume; thus, step by step, we are led to the conviction that crystalline form is inseparably connected with, and dependent upon, peculiar axial proportions.   Whatever modifies these proportions in a definite manner, must be considered as the ultimate cause of the plesimorphic differences referred to above.   In this connection, the observations of Mitscherlich, Fresnel and others, upon the application of heat to crystals, may be studied with much advantage, as they are well calculated to lead to results as positive as they are important.   According to these gentlemen, when crystals not belonging to the regular system are heated, their axes expand unequally and change the magnitude of their angles.   Crystals of the right prismatic system have their three axes expanded differently.   In arragonite, on raising the temperature from 32° to 212°, the inclination of the lateral faces increases by 2′ 46″, and that of the terminal faces diminishes by 5′ 29″; gypsum is more expanded by heat in the direction of the principal axis than in that of the lateral axes.   In bitter spar, the obtuse angle of the primitive rhombohedron diminishes when the temperature is raised from 32° to 212° by 4′ 6″; in ferruginous bitter spar, by 3′ 29″; in iron spar, containing a considerable quantity of manganese, by 3′ 31″; and in pure iron spar, by 2′ 22″.   In crystals of the rhombohedral system, the expansion is the same in the directions of the three secondary axes, but different in that of the principal axis.[*]   But the positive and methodical influence of heat in changing the density, axes and angles, and, therefore, the form

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[*] Gmelin.   Hand-Book of Chemistry, Cavendish Society edition, vol. i. p. 233.

of a crystal, is beautifully and conclusively shown in the following example: Calcareous spar, heated to 180° F., has its specific gravity decreased in the proportion of $1 : \frac{1}{1.00961}$; its principal axis expanded by 0.001961; and each horizontal axis contracted by 0.00056; in consequence of which the obtuse angles of the primitive rhombohedron diminish, and the acute angles increase by 8′ 34″. Now, according to Kopp, when its principal axis = 0.85440, and its obtuse angle = 105°.5′, the specific gravity of calc spar is 2.7220. When heated, its specific gravity becomes 2.71675, and its atomic volume passes from 232.36 to 232.80; or, in other words, a modification of form ensues.

The phenomenon of dimorphism presents us with many examples strongly confirmatory of the significant connection, here indicated, between form and capacity for heat. Still more do they conduct us to some positive notions concerning the active agency of caloric in producing crystalline form. "Crystals formed at one particular temperature," says Gmelin, "and then exposed to that temperature at which crystals of a different kind are produced, often lose their transparency, and, without alteration of external form, become changed into an aggregate of small crystals of the latter kind. We may therefore imagine that the atoms of the solid crystal displace one another in such a manner as to bring about the particular arrangement which they are disposed to assume at the altered temperature, the new arrangement belonging to a different crystalline system."[*] Carbon, as found in the diamond, which belongs to the regular system, has a different atomic heat from carbon as found in rhombohedral graphite. In fact, all the varieties of carbon differ in the same respect, as shown in the following table:

Varieties of Carbon.	Specific Heat.	Atomic Heat.	Atomic Volume.
Diamond.	0.1192 D,M.		
	0.1469 Rg.	0.8814	1.690
Graphite:			
Natural,	0.2019 Rg.	1.2114	
Artificial,	0.1970 Rg.	1.1820	2.857
Coke:			
3 varieties,	0.2036 Rg.	1.2216	
	0.2017 Rg.	1.2102	
	0.2031 Rg.	1.2186	3.333
Charcoal:			
Strongly ignited,	0.2415 Rg.		
" "	0.2009 D,M.	1.3272	
Moderately heated,	0.2964 D,M.	1.7784	
From Sugar,	0.1592 Rg.	0.8552	
" Ol. Terebinth,	0.1801 Rg.	1.0806	
Lamp Black,	0.2570 Av.	1.5420	
Animal,	0.2608 Rg.	1.5648	

Carbon thus furnishes us with an excellent example of the connection between the calorific capacity of a body and its degree of aggregation.

[*] Gmelin. Op. cit., vol. i. p. 98.

If sulphur be melted and allowed to solidify at 230° F., it assumes the form of an oblique rhombic prism; if it be made to crystallize from its solution in bisulphuret of carbon or oil of turpentine, at a temperature under 100°, it appears in the shape of octohedrons with rhombic bases.   According to Graham, the crystals of sulphur produced at the higher of two temperatures, become opaque when kept for some days in the air, and pass spontaneously into the other form, in consequence of a new arrangement of atoms; at the same time their transparency is destroyed, because a mass of crystalline particles takes the place of one crystal, thus causing the light to be refracted in various directions.   The crystals produced at the lower temperature are disintegrated and changed into the other form by a moderate heat.

As in the case of carbon, the varieties of sulphur differ in atomic heat.[*]

If chloride of calcium and carbonate of ammonia be mixed together, and the solution brought to a temperature of 50° F., the precipitating carbonate of lime will take the form of rhombohedric crystals, as in calc-spar; if the solution be kept at 150°, the crystals appear as cubes, as in arragonite.   If these cubic crystals are allowed to remain in the liquid, while the latter is gradually cooling, they are slowly but completely converted into calc spar.[†]

According to Fownes, green sulphate of iron crystallizes in two different forms, and with two different proportions of water, according to the temperature at which the salt separates from the solution.[‡]

A prism of arragonite, exposed to the flame of a spirit-lamp, decrepitates at a low red heat, and breaks up into numerous minute rhombic grains of calc spar.   Melted chalk, on cooling into marble, exhibits a rhombohedral structure.   From these facts it appears, that while a low temperature gives to CaO, CO_2 the form of calc-spar, a higher temperature is necessary to produce arragonite,—which latter is indeed formed only between very narrow thermometric limits.   Below are the atomic heats of different varieties of carbonate of lime.

CaO, CO_2	Atomic Heat.
Calc-spar,	10.0747
Artificial,	10.2515
Arragonite,	10.3575
Iceland spar,	10.5343
Chalk,	10.8474
Statuary marble,	10.8979

Carbonate of strontia precipitates in an indeterminate form, when chloride of strontium is decomposed by carbonate of ammonia in the cold.   When heated, it takes the form of arragonite.   But the chlorides of barium and lead, when mixed with carbonate of ammonia in the cold, respectively precipitate PbO, CO_2 and BaO, CO_2 in the

* Regnault. Op. cit., pp. 206, 207.   † Rose. Philosoph. Mag., 3d ser., vol. xii. p. 465.
‡ Elements of Chemistry, p. 176.

form of arragonite. Now the latter carbonates have a somewhat higher atomic heat than SrO, CO_2.

If hot, concentrated caustic potash be saturated with protoxide of lead, the latter separates in the shape of rhombic octohedrons having a yellow color; as the solution cools, however, red, crystalline scales are deposited on the first. If the red crystals be heated, they take the first form and also the yellow color.[*]

Anatase and rutile, two forms of oxide of titanium, though both belonging to the square prismatic system, have incompatible angles, which assign to each a different primitive form. They differ in atomic heat and volume.

Bisulphuret of iron, as common iron-pyrites, belongs to the regular system; as white iron-pyrites, to the right prismatic system,—the latter being of a paler yellow color and much softer. Breithaupt thinks that the former has been formed at a higher temperature than the latter. The atomic heat of the common variety is 7.5480; of the white variety, 7.8854.

Sulphate of nickel ($NiO, SO_3 7Aq.$) is trimorphous. It crystallizes below 59° F. in right rhombic prisms; between 59° and 68° F. in acute octohedrons with square bases; and above 86° F. in oblique rhombic prisms; also in forms belonging to the right, square and oblique prismatic systems. The right rhombic prisms, after exposure to sunlight for a few days, are found to be composed of square-based octohedrons, often several lines in length. The sulphates of zinc and magnesia exhibit similar phenomena. They assume different forms, according as they are made to crystallize at a high or a low temperature,—manifesting, as Mitscherlich has shown, very peculiar and interesting changes with variation of temperature.[†]

According to Frankenheim, sal ammoniac, which generally crystallizes in regular octohedrons, appears at higher temperatures to assume forms belonging to the right prismatic system.[‡]

When the rhombohedrons of KO, NO_5 are heated considerably above 100° C., they change into prismatic crystals. A hot solution of KO, NO_5 deposits prismatic crystals when slightly cooled; at a temperature of 14° F., however, rhombic crystals begin to appear. (Frankenheim.)

Protiodide (red iodide) of mercury sublimes at a low heat, and also separates from solution in square, prismatic tables of a scarlet hue; at a higher temperature, rhombic tables of a sulphur-yellow color are formed. As often as they are heated, the red crystals turn yellow, and again become red as they cool. (Gmelin.)

Examples of this kind attest the strong, controlling influence of temperature upon isomorphism. We see that whether a body shall be isomorphous with a second or a third, is mainly determined by temperature. "Les isomorphismes chimiques d'un

* Mitscherlich. Jour Pr. Chem. 19, 451. † Gmelin. ‡ Jour. Pr. Chem. 16, 3.

même corps peuvent donc changer completement avec la température."* Changes in the form of a body correspond to variations in its combined heat.

Many crystallizable bodies assume a peculiar state of aggregation known as the vitreous condition, which may be considered as a variety or modification of dimorphism. The binarseniate and biphosphate of soda resemble each other strongly in physical and chemical properties. When exposed to the same heat, the first solidifies, on cooling, into a white opaque mass composed of interlaced crystalline fibres, while the second is converted into a transparent, colorless glass. While undergoing these changes, the arseniate discharges sensibly more heat than the phosphate; hence, probably, the glassy condition of the latter salt is due to the retention around its particles of a portion of the heat of fluidity.†

Ordinarily sugar has a granular or crystalline structure. When melted and allowed to cool slowly, it assumes a glassy condition and manifests very different physical properties. If, while still soft and viscid, (as at the temperature of 100°.) it be rapidly drawn out into threads, a large quantity of heat is liberated, and the sugar separates into minute granules of a pearly lustre.

That the vitreous condition is in some manner connected with the amount of heat accumulated around the ultimate particles, is shown by the fact that glass kept soft for a long time, gradually loses its heat and is converted into a substance known as Reaumur's porcelain, in which it assumes different characters. The crystalline and amorphous states of the same body differ to a certain extent in their properties; the former being in general harder, specifically heavier and less soluble than the latter, in which the atoms are placed farther apart than in the first. Graham also affirms that the amorphous condition is accompanied by a larger quantity of combined heat than the crystalline.

Arsenious acid sublimes as a transparent glass with a light, yellow tint. By exposure, the vitreous mass gradually changes into a congeries of small octohedral crystals, and becomes opake, milk-white, and slightly altered in solubility and density. According to H. Rose, if the vitreous mass be dissolved in hydrochloric acid, each crystal as it separates emits a flash of light. Regnault, in his second memoir, says, "l'acide vitreux (arsenious) devient promptement opaque à la température de 100°." The vitreous acid has an atomic heat of 15.0796; the opaque, 15.2064. Now, Guibourt has shown that the specific gravity of the vitreous acid diminishes during the change to the opaque form, from 3.785 to 3.695; and that the latter dissolves rather more abundantly both in hot and cold water than the transparent. This is an exception to the ordinary cases, for the change from the amorphous to the crystalline form is accompanied generally with increased density and diminished solubility. It is interesting here to observe that the difference in atomic heat, though very small, is

in favor of the opaque variety—another departure from the usual rule, the opaque form, having commonly less than the transparent or vitreous.

The limits to which I have assigned this paper, prevent me from here introducing in detail many facts similar to the above. I would, however, especially refer the reader to the first volume of Gmelin's Chemical Hand-Book, where, in the article on Amorphism, have been collected from the writings of Rose, Fuchs, Regnault, Frankenheim, Marchand, Scherer and others, many valuable and instructive examples of the modifying influence of caloric upon the state of aggregation, form and properties of bodies. These constitute but a few of the many examples which a progressive science is daily placing upon record, to be used hereafter for the loftiest purposes of philosophical generalization. They are worthy of, and will amply repay, the closest investigation, since they conduct us to the very threshold of Nature's secret laboratory, promising to lay bare that for which the human mind, through all ages, has so fondly and unceasingly longed—a knowledge of the primary physical cause of all natural phenomena.

Nature annually performs for us, on a grand scale, an experiment at once simple, beautiful and instructive. I allude to the formation of snow crystals. In this process the crystallizing material is the same throughout all the varieties of form, but the accompanying temperature varies. In his excellent work on the Arctic Regions, Scoresby has classified the many forms of snow-flakes observed by him in his voyages to the North, and given a table showing the different temperatures at which different crystals were seen to fall. He refers the varieties of snow crystals, for their cause, to variations in atmospheric temperature. My own observations made during the past winter, lead to the same conclusion. When, after variable weather in the winter season, the cold has set in steadily for several days, gradually condensing the aqueous vapor and obscuring the heavens, the wind constantly blowing from the same point, and the upper atmospheric currents, as shown by the course of the clouds, having the same direction as the lower, I have very generally found that while the thermometer indicates nearly the same reading, the crystals of snow that fall under such circumstances have the same or but slightly differing forms. Any marked change in the height of the mercurial column is very commonly followed by some manifest change in the snow-figures. It is true that very different and unrelated forms are often observed to fall simultaneously; but reasons well known to the climatologist, render it very probable that they have been generated in atmospheric currents or strata differing in temperature. Indeed I suspect that a snow-crystal, by passing through variously heated currents of air, may have its form considerably altered as it descends towards the earth. By holding the partly-closed hand over a crystal, so as to increase the warmth of the surrounding air, I have, on several occasions, noticed very remarkable modifications of form. Mr. James Glaisher also speaks of this phenomenon, in

a communication directed to the Editor of the Illustrated London News, (Feb. 24th, 1855.) He says, "In conclusion, I may be forgiven if I remark, for the benefit of the inexperienced, that the crystal subjected to the warm influence of the proximity of the observer, not unfrequently alters in form before it sensibly begins to melt. I have myself more than once drawn a specimen on its first descent, verified it to my satisfaction, and passed on to others; after the lapse of perhaps a quarter of an hour or more, I have been surprised by witnessing, as I imagined, a new specimen occupying the precise spot of the former. In each case, however, careful observation proved to me that it was no other than the crystal I had already drawn, and that the dissimilarity arose from a general simplification of the figure caused by the subsidence of the groups of prisms surmounting the apex of the rays, the rounding of the edges of those prisms which remained, the subsiding of two or more prisms into one, and the elongation of spiculæ which formerly served as the axes of prisms."

Very peculiar changes may be witnessed by studying the gradual wasting of a snow crystal in consequence of an increasing warmth of the air. Thus I have seen a hexagonal lamella similar to fig. 87 of Scoresby's plates, change into one like fig. 28, then resemble a star, (fig. 13.) and ultimately leave only its three axes as the skeleton or fundamental portion upon which the body of the crystal was erected. These axes finally disappeared, the destruction beginning at their apices and ending at their common centre or junction, thus following an order the reverse of their formation. An exact statement of the amount of heat combined with each variety of snow-crystal would constitute a valuable addition to our present stock of knowledge.

Thus, then, we learn that the particular system or genus in which a body crystallizes, is mainly determined by the temperature at which solidification takes place.

Dimorphism is intimately associated with isomerism. Both phenomena furnish us with instances of the positive and active relation which atomic heat bears to both the form and properties of bodies. Some isomeric substances, though agreeing in ultimate ponderable compositions, differ completely in atomic weight, and every other respect; in others, both the atomic weight and elementary compositions are the same; in others the atomic weights are the same and their molecular arrangement different; but, in all, as far as I can ascertain, their atomic heats are different. Phosphoric and pyrophosphoric acids are alike in composition but dissimilar in properties: the second acid is simply the first in a state of fusion. Racemic and tartaric acids are very similar in properties and chemical relations, and, according to Mitscherlich, isomorphous. When heated, they each form three classes of salts, but are so modified that each, upon uniting with the same base, in the same proportion, produces a different compound. When destructively distilled, both give rise to the same pyr-acid. It is well known, that every organic acid has its corresponding pyr or fire acid.

"When the group of chemical molecules are differently arranged," says Kane, "the

various differences in color, density, solubility and figure which belong to dimorphous bodies are produced; but when the difference of arrangement extends to the chemical constituents of these molecular groups, independent but isomeric bodies are produced."[*] It would thus appear that isomorphism, dimorphism, polymorphism and isomerism are immediately dependent upon a peculiar arrangement of atoms, and of molecules composed of two or more atoms. From the inherent tendency to such arrangement, probably results the binary method of combination in both the organic and inorganic worlds. Now, from all the foregoing facts, we have seen that when bodies agree in form and properties, they also approximate in atomic heat. When bodies assume two or more forms, their chemical properties differ, as do also their atomic heat. Bodies having the same composition, but differing in structure (as in all probability isomeric bodies do), and consequently in properties, differ also in atomic heat.

Throughout this series, a remarkable parallelism is evident, between atomic heat on the one hand, and arrangement of atoms, and forms and properties of bodies on the other. It is very generally true, that bodies having the same form, have also the same properties; and that difference of form is accompanied by corresponding difference in properties. Very probable is it, therefore, that not only form, but also color, specific gravity, solubility, hardness, &c., are all dependent upon certain arrangement of atoms. But the arrangement of particles, necessarily pre-supposes an arranging or motor agent, which constitutes the ultimate physical cause of crystallization. As the attractive force, so grandly displayed in the solar system, must ever be present and in action among the planetary bodies of that system, that they may be retained in their accustomed orbits; so the atoms of a crystal require the continued presence and equal action of the arranging power, to maintain them in that relative position necessary to the preservation of the general form. Hence we infer, that the arranging cause must be a motor power, and always present. Furthermore, if it can be shown that such an agent exists in a crystal, a strictly logical method should prevent us from seeking elsewhere for the cause of peculiar atomic arrangement, and all the physical phenomena manifestly dependent upon it.

Now we have seen that caloric is always associated with the ponderable matter of a crystal, and that it is positively related to crystalline form, and hence, to arrangement of atoms upon which form depends. It only remains to adduce some proof of its efficient activity. The experiments of Fresnel,[†] Baden Powell,[‡] Addams[§] and others show conclusively that heat is self-repellant. Moreover, a careful analysis of the entire series of phenomena, which, in the aggregate, constitute the natural history of caloric, tends strongly to establish the fact that heat is a most powerful motor agent. Indeed, the ancients, with very few exceptions, contended (vaguely, however, and un-

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* Elements of Chemistry, p. 231.   † Annales de Chem. et de Phys. 29, 57, 107.
‡ Philosoph. Mag. 18, 415.   § Gmelin's Chemistry, vol. i. p. 212.

supported by experimental proof,) that caloric was the prime mover and cause of all natural phenomena. A forcible writer of our own time and place, maintains this doctrine with an imposing and comprehensive array of argument.*

The following brief resumé of facts, connects itself with the question under consideration :—

Cohesion varies inversely with the temperature, generally increasing as the latter diminishes, and vice versa. Heat expands bodies, rendering those that were hard, soft and even liquid and gaseous. This change in bulk and condition, corresponds to an increased separation of atoms. A sufficient reduction of temperature solidifies all bodies. Liquids and gases may be regarded as solid matter, plus a certain amount of caloric, the amount varying with the species of matter. Otherwise, the particular temperatures at which bodies undergo these changes would not be so very different, nor would they always be constant for the same body. Heat is certainly the cause of fluidity, gasefaction and evaporation. The most permanent gases—those which manifest the greatest resistance to being deprived of the gaseous form, by external pressure and cooling—are those in which the most intimate union exists between the ponderable matter and heat. Gases contain more heat than liquids, are more elastic, therefore, and manifest a tendency to expand without limit, if not opposed by external obstacles; liquids contain more heat and are more mobile than solids, which contain least of all the forms of aggregation. Gases by their refinement, superior activity and expansive power, pass through openings impervious to liquids; so liquids escape through openings impassable to solids. Ponderable matter is made to occupy a larger or smaller space, according as it is combined with more or less of the repellant material—caloric.

Dr. Black, whose researches may be considered as constituting the foundation of the science of thermotics, showed, quite clearly, that the structure and properties of solids varied according as their combined heat was increased or diminished. According to this observer, the malleability and ductility of metals depend upon the quantity of latent heat they contain. When hammered, they become red hot in consequence of the disengagement of heat; at the same time, while their density, and consequently specific gravity increase, their malleability diminishes and they become brittle. Malleability is restored by heating. In the first volume of his valuable Hand Book of Chemistry, Gmelin has given numerous and very striking instances, showing that heat imparts to many ponderable bodies particular colors, which vary according to the quantity of heat contained in the bodies. Those metals which increase most in specific heat, when exposed to an elevated temperature, are found to have their rate of expansion also most rapidly increased. According to Dulong and Petit, when the

*Dr. S. L. Metcalfe, Caloric, its Agencies in the Phenomena of Nature.

increased capacity for heat is about one-tenth, the increase in expasion amounts to one-hundredth. But we cannot conceive of this expansion taking place without the atoms being moved farther apart, thus increasing the volume. Coincidently with this change, and as a proof of its reality, we find the specific gravity of the metal diminished. Hence it is, that the capacity for heat of any body increases with the temperature; for the arrangement of the atoms at greater distances from each other must necessarily afford more space for the accumulation of caloric around the particles. Thus the specific heat of copper is reduced, by violent hammering, from 0·095 to 0·935; but raised again by ignition, to 0.0949. Lead and tin, on the contrary, which do not increase in specific gravity under the die, likewise suffer no diminution of specific heat by pressure. The specific heat of soft bell-metal, (Cu_{80} Sn_{20}) which has a density of 8·6843 is 0·0862, while the same metal hardened, in which state its density is 8·5797, has a specific heat of 0·0858. (Regnault.) The more dense a body is, the greater is its specific gravity and the less its specific heat. A beautiful example is given by Regnault in the case of precipitated silver. The specific heat of this substance varies with the degree of condensation, as shown by the following results determined by the method of cooling :—

	20° to 15°	15° to 10°	10° to 5°
Very little pressed,	0·08535	0·08441	0·08519
More strongly " . . .	0·05844	0·05772	0·05781
Still more "	0·05749	0 05713	0·05749
Strongly hammered and rubbed,	0·05634	0·05671	0·05654
More strongly " "	0·05616	0·05624	0·05650

Peroxide of iron and peroxide of nickel when strongly ignited, increase in density and diminish in specific heat. The varieties of carbon present the same result. The interesting experiments of Messrs. Hopkins, Fairbairn and Joule, upon the effects of extreme pressure, demonstrate that the temperature of fusion increases in proportion to the pressure to which the fused mass is subjected. In employing a pressure of about 13,000 lbs. to the square inch, on bleached wax, they found that increase in the temperature of fusion was not less than 30° F., about one-fifth of the whole temperature at which it melts, under the pressure of the atmosphere.* Such facts, I may say in passing, militate strongly against the generally received, though probably erroneous theory of the exalted calorific condition of the centre of our planet.

But the active agency of caloric in affecting specific gravity, is seen by comparing compound bodies with the elements of which they are composed. Thus hydrogen and chlorine unite, without condensation, to form hydrochloric acid gas. The specific gravity of one volume of hydrogen is 69·26; of one volume of chlorine, 2421·6; and of one volume of hydrochloric acid gas, 1247·4; the mean of the two former numbers. The specific gravity of hydrogen is about 36 times less than that of chlorine; its

* President Hopkins' Address before the 23d Annual meeting of the British Association.

elastic force, on the contrary, is exceedingly great; while cold alone, or a pressure of but four atmospheres is sufficient to condense chlorine. The expansive power of hydrochloric acid gas, is equal to the pressure of 40 atmospheres, at the temperature of 50°. Now the atomic heat of H is 21·2064; of Cl, 14·4627; and of HCl, 28·9263. Four volumes of HCl must contain as many atoms as two volumes of H, or of Cl; or, two volumes of HCl contain as many atoms as one volume of H or Cl. But one volume of H contains half an atom. hence one volume of HCl must contain one-fourth of an atom, which must therefore be surrounded by twice as large a heat-sphere as the half-atom of H. Such facts authorize us to conclude, that chlorine in combining with hydrogen has its specific gravity reduced, in consequence of abstracting from the latter gas an additional quantity of caloric, by which its particles are separated further from each other and made to occupy a larger bulk. This supposition will also account for the change in elasticity. The union of iodine, bromine, cyanogen, &c., with hydrogen is accompanied by a similar reduction in specific gravity, and alteration in physical and chemical properties. When hydrogen unites with sulphur, phosphorus, and arsenic-vapors, and with carbon, in different proportions to form, respectively, sulphuretted, phosphuretted, arseniuretted, and light and heavy carburetted hydrogen gases; with oxygen to form aqueous vapor, and with nitrogen to produce ammonia, the resulting specific gravities of these respective compounds is very much less than the sum of those of their constituent elements. The volume and elastic force of these gases are also altered in a remarkable manner.

According to Graham, the more nearly bodies agree in composition, they are the more likely to act as solvents of each other, or to be miscible in the liquid form.* But we have seen that in both compound and elementary bodies of the same atomic constitution and of like chemical constitution, the specific heats are in the inverse proportion to the atomic weights. In this connection, I may refer to those numerous and interesting examples of change in the solubility of bodies after being heated. although their composition remains the same. Alumina, binoxide of tin, sesquioxide of chromium, and other metallic peroxides, and certain salts, such as silicates, tungstates, phosphates, antimoniates, &c., after exposure to a temperature just below redness, lose their solubility in acids. In its cubic form, the bisulphuret of iron resists the action of both air and water; but in its right rhombic form, when exposed to moist air, it absorbs oxygen with great avidity, and is converted into a crystalline mass of copperas.† Spontaneous ignition often accompanies those changes in solubility, and generally just as the body is passing from the soluble to the insoluble state. "Je crois même que ce changement de chaleur spécifique correspondant à un changement d'agrégation, donne l'explication d'une phénomène bien connu des chimistes et des physiciens, je veux parler de l'incandescence qui se manifeste subitement dans certains

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* Elements, p. 142.   † Kane.

oxides, quand on les soumet á une chaleur graduellement croissante. Il sa produit alors un changement dans la disposition moléculaire du corps, un changement d'agregation qui se manifeste dans les caractères chimiques. En effet, la substance qui etait facilement soluble dans les acides, avant son incandescence, est devenue très difficilement soluble, quelquefois même insoluble après. L'incandescence s'explique facilement par une diminution subite dans la capacité calorifique du corps, qui dégage instantanément de la substance une quantite considérable de chaleur qui auparavant était latente : cette chaleur, au moment où elle devient libre produit nécessairement une élevation thermométrique qui porte pendant quelques instants la substance á l'incandescence, quand elle n' était encore portée qu' au rouge sombre par la chaleur extérieure."*

In the *Annales de Chimie et de Physique*, (1er sér. t. 70, p. 407,) Gay-Lussac has published some observations upon certain bodies whose solubility he shows to be determined by temperature alone. These observations lead, moreover, to the supposition that all spontaneous precipitations are due to differences in temperature.

Many elementary bodies in uniting to form compounds, suffer a contraction in volume. Now, M. Filhol has shown, that in those compounds whose chemical properties are very analogous, the co-efficients of contraction are sensibly the same.† Analogous properties seem to be associated with analogies in calorific condition.

It would be superfluous to adduce other examples of the active character of caloric.

From the laborious and carefully conducted experiments of many eminent physicists, we may infer that in the most, if not all bodies, the combined heat varies to a greater or less extent in different specimens. Examples of this we find in carbon, sulphur, &c. Accompanying this variation, and in all probability caused by it, we find a change in form, condition, physical and chemical properties and the like. Indeed it is difficult to conceive how any change, even the slightest, in the heat of a body, could be unaccompanied by some alteration in the ponderable matter. The extreme sensitiveness of heat or caloric is evinced in every chapter of its endless history. It is very rational to suppose, therefore, that the influence of caloric in moulding ponderable matter into definite forms, must in a certain measure vary with the degree of aggregation of the body, which state of aggregation is indeed in great measure contingent upon the amount of caloric itself. Increased aggregation is generally an indication of diminished calorific capacity. In colcothar and the diamond we have beautiful examples of this fact. In condensing very strongly, a body often completely loses its most characteristic chemical properties. Heat acting upon two dissimilar pieces of metal soldered together, gives rise to electrical phenomena : acting upon water, produces motor effects. From such conspicuous examples we are forced

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* Regnault, Ann. de Chim. et de Phys. 3me Sér. i. 188--9.
† Annales de Chim. et de Phys., 3me sér. t. xxi., p. 415.

to conclude that any variation in the ponderable substratum or medium upon which a definite amount of caloric is made to act, or in the attending circumstances by which the body is surrounded, must necessarily produce a variation in calorific effects. Hence the want of absolute identity in the crystalline form of many bodies which are really isomorphous. Hence, too, the discrepancies occasionally met with between the atomic volume of a body and that of the other members of the group to which it belongs. For atomic volume is calculated from relative weight and specific gravity; as the latter two vary, so must the former. Now the specific gravity of a body may vary according as it is adulterated or not with matters lighter or heavier than itself, and having naturally different quantities of heat; or the body itself may, in different states, possess different quantities of combined heat. This view will explain the fortuitous coincidences in form accompanying dissimilarity of properties and composition; and, also, why certain elements manifest isomorphism in their analogous compounds, and yet cannot be shown to be isomorphous in their elementary state. For the mathematico-chemical investigations of Kopp lead us to suppose that the primitive atomic volume of an element suffers a considerable change in its different combinations,—the combining volume bearing in most instances a simple or multiple relation to the primitive. Hence a body may have two or more atomic volumes as well as crystalline forms, which, indeed, we should infer à priori.

We know very well that a certain elevation of temperature may so affect the molecular structure of a body as to destroy its identity or individuality,—changing its form, color, properties, &c. This molecular change is nearly always accompanied by a simple multiple change in the equivalent of a body, and of course in the atomic volume. It seems very probable, therefore, that the different forms which certain elementary bodies are known to assume, are intimately connected with diversity of equivalent volume. We may suppose that sulphur has a larger and more intricate volume when it takes the complex form of bisulphate of potassa, than in its ordinary simple form. So, likewise, we may suppose that when one equivalent of chlorine replaces one of cyanogen, or two of manganese in combination, it must have a varying volume, and consequently a varying form, in compound bodies. According to Graham, the tendency of discovery is to bring all the elements into one class, either as isomorphous, atom to atom, or with the relation to the others which sodium, chlorine and arsenic exhibit. In this connection, the sameness of atomic heat of the elements, the similarity of many of the atomic volumes, and the simple relationship of the others, as shown in the table, are significant facts.

If we ignore the materiality of heat, and deny that it is as essential to the composition of bodies as ponderable matter itself, the changes in form, properties, &c., which these bodies undergo, are without explanation. If, on the contrary, we follow the evidence of our senses, and acknowledge the substantiality of caloric and the extent

and dignity of its influence upon the self-inert bases with which it is combined, we open a channel for the hopeful investigation of cause and effect. Changes in the properties of things must be preceded by compositional and structural changes, either of their ponderable or imponderable element, or of both, just as in the animate world organic derangement is the invariable antecedent to functional disturbance. If caloric be merely a property or quality of matter, it cannot possess that self-active and causative power which a careful analysis of its history warrants us in assigning to it. If it be a substantive entity, we can readily understand the remarkable constancy and mathematical precision of its effects; and we can understand, furthermore, how its presence or absence in certain quantities can produce those structural or molecular alterations which manifest themselves externally in variations of form, specific gravity, color, solubility, &c. The estimation of the absolute amount of heat combined with bodies in their different states of aggregation, is one of the most difficult problems in physical science;—and one of the most important, since upon its solution depends the explanation of many unexplained and apparently inexplicable phenomena. However, if we bring together the few reliable observations that have been made in this channel, (especially those concerning the relation between the calorific condition and refractive power of substances,) and the numerous collateral facts which are scattered throughout the literature of physics, we will have material sufficient to begin already the work of cautious and satisfactory generalization.

The following conclusions, as being more or less probable, seem to flow naturally from the foregoing facts and arguments :—

1. That no invariable connection exists between the form and ponderable atomic constitution of a body.

2. That form is immediately dependent upon peculiar axial proportions, which are themselves the results of a certain molecular arrangement.

3. That the arrangement and disarrangement of atoms implies a motor agent; while the definite and constant relation between changes in aggregation and variations in form, implies the materiality of this agent and its continued presence, whether in the same or varying quantities.

4. That this agent has periods of action and periods of rest.

5. That caloric is a positive material entity—an essential element in all bodies, always present in different proportions.

6. That caloric is self-repellant and endowed with great physical power.

7. That crystalline form is the visible representative of atomic volume.

8. That isomorphous bodies have sensibly the same atomic heat and the same atomic volume.

9. That in elementary and compound isomorphous groups, the numbers indicating atomic heat and volume are simply related.

10. That two or more atoms of one element may replace one of another, and retain the same figure; and vice versa; hence, equal numbers of atoms are not essential to isomorphism.

11. That similarity of constitution is generally, though not always, accompanied by sameness of combined heat.

12. That at certain temperatures, the elements may all be made to assume the same form.

13. That variation in the atomic heat of a body is accompanied by variation in its form.

14. That atomic heat is the cause of isomorphism and polymorphism,—consequently of crystalline form in general.

Is caloric, through its affinity for, and active influence upon ponderable matter, the primary physical cause of all crystallization?